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QUALITY CONTROL OF POLYMER COMPOSITE MATERIALS BY FAR-INFRARED LASER LIGHT SCATTERING

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ABSTRACT

Filler distribution and orientation in reinforced polymers is an important technical problem. A number of infrared techniques for the industrial inspection of reinforced polymeric films, including infrared spectroscopy, laser scanning and infrared thermography are described in this paper. The attenuation and polarization properties of a far-infrared laser beam after transmission through the film are shown to correlate with the concentration and distribution of fillers, while being relatively unaffected by small-size inclusions. Examples of applications to the inspection of mica-filled polyethylene, as well as of natural fibers in lumber, are presented. Infrared thermography techniques for the inspection of opaque materials are also described.

INTRODUCTION

GLASS AND MICA-FLAKE REINFORCED PLASTICS are increasingly used as inexpensive and easily formed materials with superior mechanical properties as compared to homogeneous polymers. U.S. sales of fillers and reinforcements in 1985 were as high as 2.6 million metric tons, and show a remarkable growth rate which is expected to average in the 9-12% range over the next decade[1]. The toughness and strength properties of polymer composite parts after forming processes such as extrusion and molding are substantially dependent on the microstructural properties of the compound, and in particular on particle dispersion and preferential directions of orientation within the matrix.

The evaluation of filler properties and distribution is presently made mainly by manual sampling and microscope inspection, followed by statistical analysis. The accelerating industrial trend toward unsupervised computer-controlled production, as well as the increasing requirements of quality assurance programs, ask for a real-time, automated quality control of the product during production. Noncontact methods are required to continuously evaluate the microstructural characteristics of the formed material for on-line quality assessment and for statistical process control purposes. Optical techniques are an attractive approach for such applications because they are effective and noninvasive. Different portions of the EM spectrum, from microwaves to gamma-rays, (see Fig. 1) may be used for material characterization purposes. In this paper we report on the use of far infrared (Far-IR) laser radiation, in the 50 to 1000 μm spectral range between infrared and microwaves, for polymer composite characterization. Applications to the analysis of filler concentration and dispersion, orientation, and form birefringence will be described and discussed.

INFRARED SPECTROSCOPY ANALYSIS

Infrared (IR) spectroscopy has been used for a long time for the characterization of polymeric materials[2]. Examples of on-line spectroscopic analyzers are moisture sensors, chemical composition and contamination analyzers[3]. Advantages of IR spectroscopy are a good analytical power thanks to the detailed spectral contents, the possibility to finely focus the probe beam resulting in a fine spatial resolution, and the availability of relatively strong light sources and of sensitive detectors.

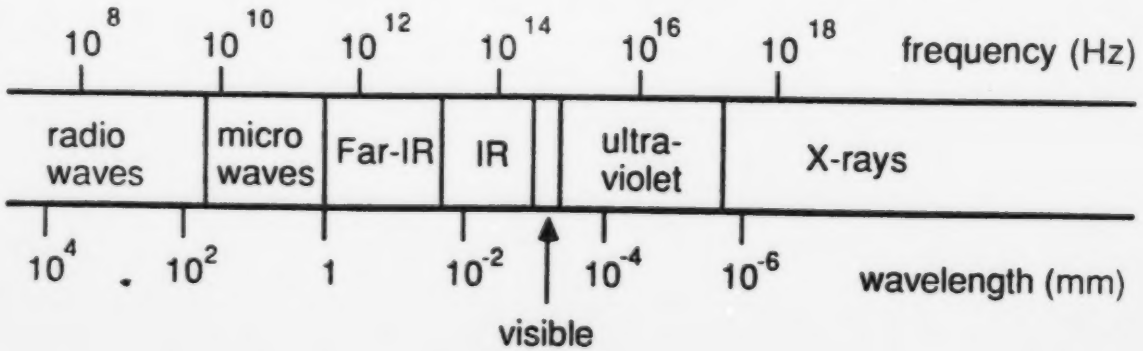

Fig. 1 The spectrum of electromagnetic waves.

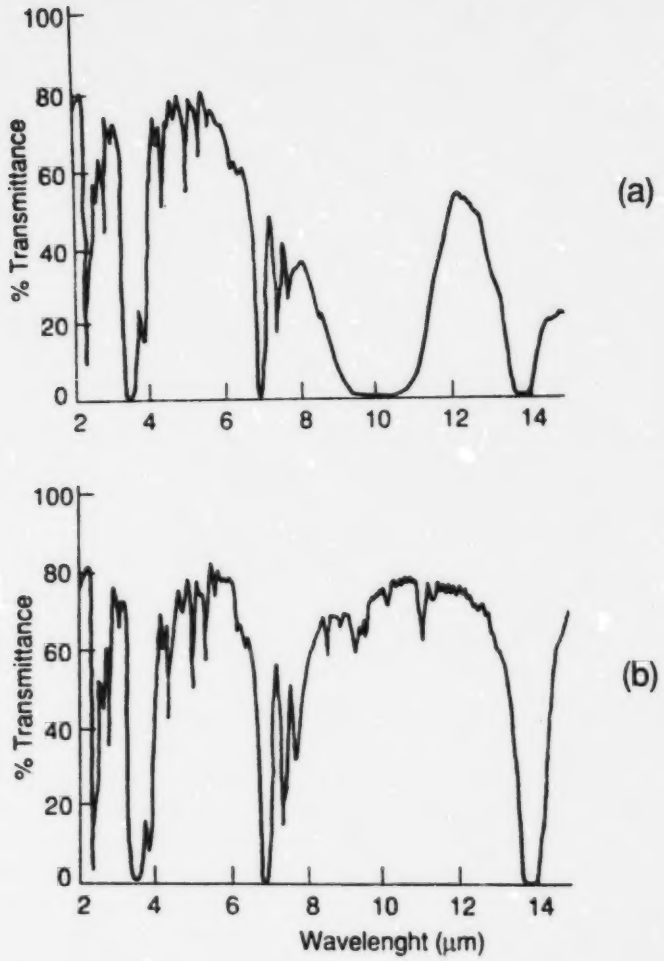

Fig. 2: IR transmission spectrum through a polyethylene film (a) with and (b) without mica filler.

The concentration of mica fillers in reinforced polymeric sheets may be evaluated by IR spectroscopy. Figure 2 shows the IR transmission spectra through a nearly 0.3 mm-thick polyethylene (PE) film (a) with 10% dispersed mica flake concentration and (b) without mica fillers. The wide absorption band by the mica material in the λ = 10 μm spectral region is quite visible. By taking the ratio between the transmittances inside and outside of the absorption band, and using Beer's law, one can evaluate the mica concentration in the illuminated volume of the film. However, the extermely strong absorbance by mica in the 10 μm region, as shown in Fig. 2, makes the evaluation of such a ratio difficult. Moreover, scattering by bulk inclusions such as pigments or air bubbles within the film may significantly decrease the level of light transmittance through relatively thick

films. For the inspection of lossy materials, microwave transmittance sensors are often preferred, at the cost of a lower spatial resolution, smaller signal-to-noise ratio (SNR) and a much increased difficulty to handle and focus the electromagnetic beam[4].

An emerging technique which is intermediate between infrared and microwave is far-infrared analysis, using wavelengths in the 50 to 1000 μm range. Such wavelengths provide deeper penetration that the near- or medium-range infrared wave-

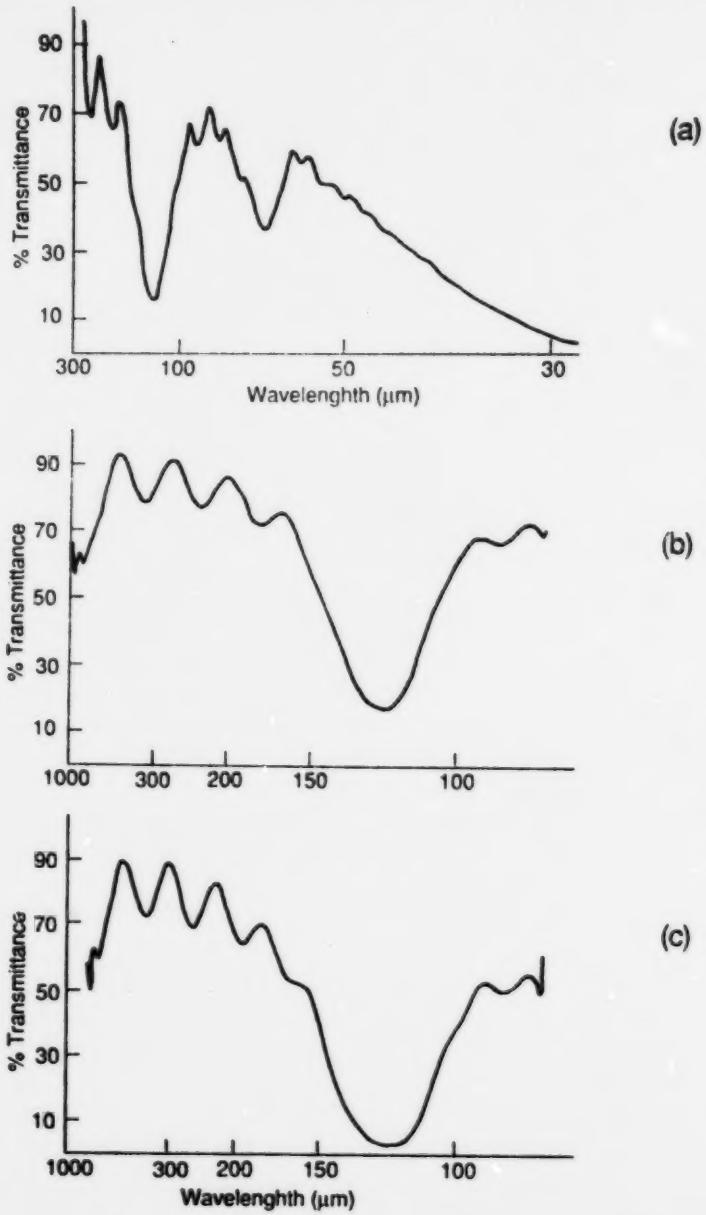

Fig. 3: (a) Far IR transmission spectrum of a polyethylene film with mica filler; (b) detail of the spectrum with 10% filler concentration; (c) spectrum of a 16% mica concentration film.

lengths, while maintaining the good optical collimation capabilities as well as a conveniently high generation and detection efficiency which are lost with microwaves. Applications of far infrared to the analysis of a number of compounds using laboratory spectrometers have been reported[5,6].

Fig. 3 shows some Far-IR transmission spectra obtained with a Bomem DA3 Fourier Transform Far-IR spectrometer through a mica filled, 0.3 mm-thick PE film. This spectrometer uses a mercury arc lamp as the light source and a cryogenically cooled Ge bolometer as detector. Figure 3(a) shows clearly the presence of two mica absorption bands at nearly 65 and 100 μm. It can be seen that the absorption coefficient is much lower in this case as compared to the infrared band in Fig. 2. Consequently, the Far-IR bands are more appropriate for concentration analysis in relatively thick films. Figure 3 also shows the effect of a variation of filler concentration on the depth of the absorption band. By applying Beer's law to the ratio between the transmittance within and outside of the absorption band, the filler concentration may be evaluated from such spectral profiles.

FAR-IR LASER ANALYSIS

Far-IR spectroscopy is not a convenient technique for transfer to the in-plant industrial environment. The relatively low output power for Far-IR light sources, together with the large amount of background thermal emission in this spectral range results in a very low SNR requiring long integration times and accurate shielding. Delicate cryogenically cooled detectors are required for the detection of the spectrally modulated beam, introducing maintenance requirements which are hardly acceptable in an industrial setting.

A more convenient approach is spectral attenuation analysis using a Far-IR laser. The experimental apparatus is shown in Fig. 4. A CH_3OH waveguide-type submillimeter laser pumped by a pulsed CO_2 laser was used to irradiate the mica-filled PE samples. The Far-IR laser pulses had typically 1 mJ of energy and 0.5 ms of duration. TPX lenses L_1 and L_2 were used to focus the beam on the sample and on the ambient-temperature Golay detector D_1 respectively. The reference detector D_2 is used to normalize the transmitted or reflected signal. By tuning the laser to different emission lines using an intra-cavity grating, the attenuation of the transmitted beam may be measured at a number of discrete wavelengths.

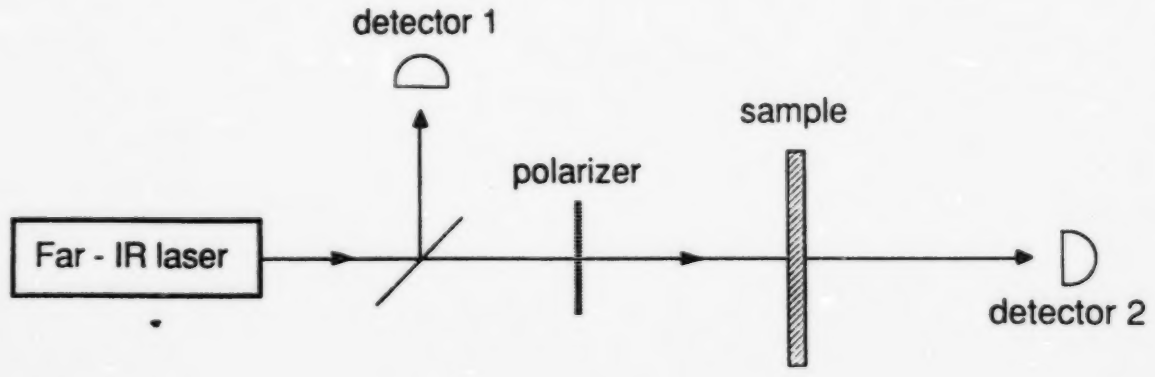

Fig. 4: Experimental apparatus for mica concentration evaluation using a Far-IR Laser.

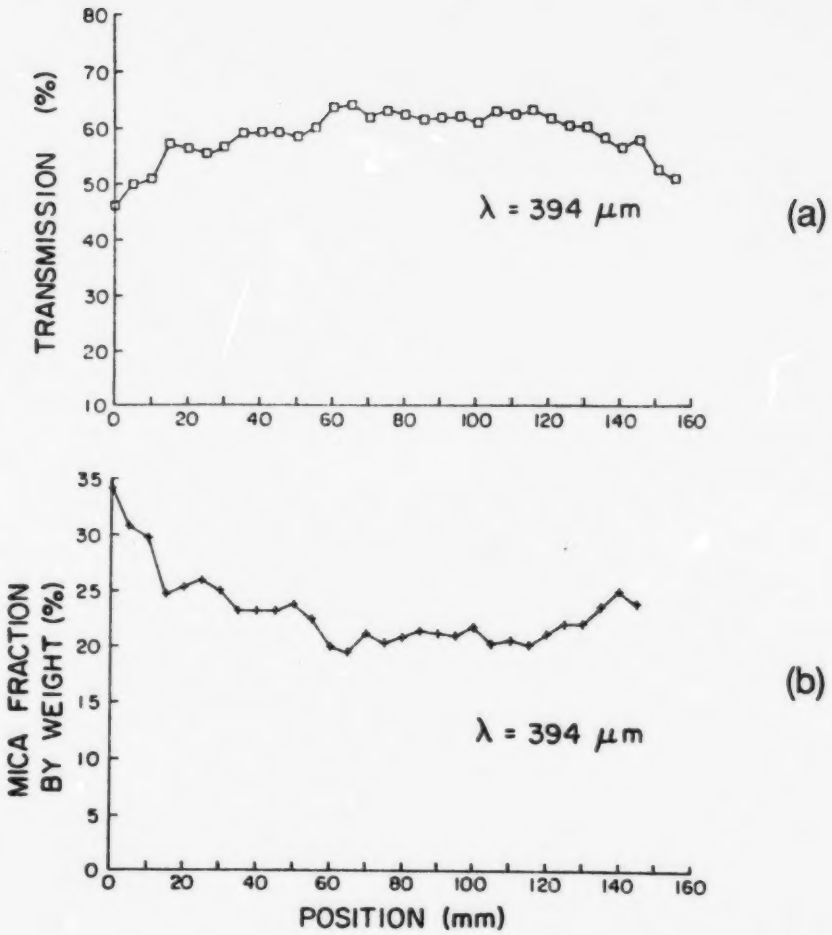

Fig. 5: Analysis of filler dispersion uniformity by spatially scanning the PE-mica sample with a focused Far-IR laser beam: (a) transmission profile, (b) evaluated mica fraction across the sample.

Fig. 5 shows a typical transmittance profile obtained by translating the PE-mica sample under the 10 mm-diameter, λ = 394 μm focused laser beam. The corresponding mica concentration evaluated by using Beer's law is also shown in this figure. Such concentration profiles are important to verify if the mica flakes are well dispersed in the polymeric matrix, or if short-range flocculation of mica particles is taking place.

Another application for Far-IR laser transmittance analysis is the evaluation of filler orientation. As mentioned above, filler orientation may significantly affect the mechanical properties of the reinforced material. An analysis of the average orientation of the mica platelets with respect to the sheet surfaces is a particularly difficult task to perform in a nonintrusive manner. The approach described here makes use of a linearly-polarized far-IR beam at different angles of incidence.

If the laser is incident at an angle θ on a polyethylene-mica sheet containing disk-shaped mica platelets parallel to the sheet surfaces, the projected mica-flake surface becomes elliptical, with one axis (in the direction normal to the plane of incidence) equal to the mica-flake radius and the other axis (in the direction parallel to the plane of incidence) reduced by a factor cos θ, as figure 6(a) shows. If a far-IR beam with wavelength much larger than the mica-flake radius is incident on the plate at an angle θ, the polarization component parallel to the longer axis will thus suffer a larger attenuation from the mica platelet than the component parallel to the shorter axis.

The experimentally obtained transmission of a far-IR beam through a polyethylene-mica sheet vs. the angle of incidence θ for an optical polarization parallel or perpendicular to the plane of incidence is shown in figure 6(b). The attenuation suffered by the perpendicular component (which sees a constant flake radius) increases with the angle because of the longer path through the sheet. The parallel component suffers a much smaller attenuation at large angles of incidence because of the reduction of the projected flake size. When the effect of the sheet thickness and of the polarization-dependent reflection losses are taken into account, the absorption coefficient for the parallel-polarization component decreases sharply with the angle while the perpendicular component is roughly constant, as figure 6(c) shows.

Similar polarization-dependent attenuation measurements can be made to evaluate the degree of orientation of fiber filled materials. Fig. 7 shows an application to the analysis of a naturally oriented material, a 0.7 mm thick pine wood sheet. By rotating the angle of polarizer, a strong degree of dichroism can be noticed. Variations in the material density, such as the presence of a node in a sandwiched wooden laminate, can be detected by scanning the laminate longitudinally, as shown in Fig. 8.

INFRARED THERMOGRAPHY ANALYSIS

Transmittance analysers are only possible for partially transparent, or translucent, materials. In many cases, composites contain highly opaque fillers, such as carbon or metal fibers, in order to improve their mechanical strength or increase their electric conductivity to avoid static charge buildup. Another approach can be chosen in this case to evaluate filler concentration, distribution or orientation by local spot heating and thermographic imaging.

A typical experimental setup is shown in Fig. 9. The inspected part is spot-heated by a narrow laser beam or other point heat source, and the heat-propagation pattern is analyzed by an IR camera. If the material is oriented, such as a unidirectional graphite-epoxy sheet, an elliptical thermal pattern will be observed, with the ratio between the two principal axes (b/a) being related to the square root of the thermal diffusivities in the longitudinal and transverse

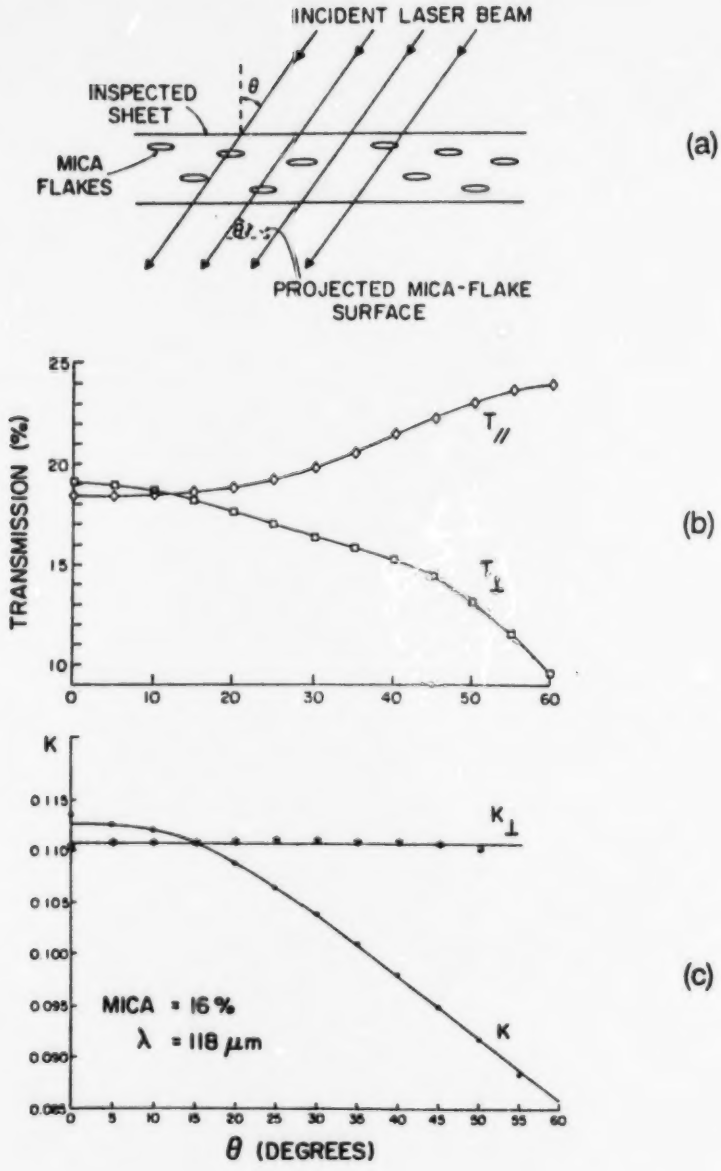

Fig. 6: Polarization effects on a Far-IR beam of a polymeric film with oriented filler: (a) schematic diagram, (b) polarized transmission vs. angle of incidence, (c) dichroism effects of a mica-filled sample.

directions. This may be used to evaluate the orientation of extruded or molded parts, or the relative thermal conductivities of the filler and the matrix in a composite, which differ by typically two orders of magnitude[7].

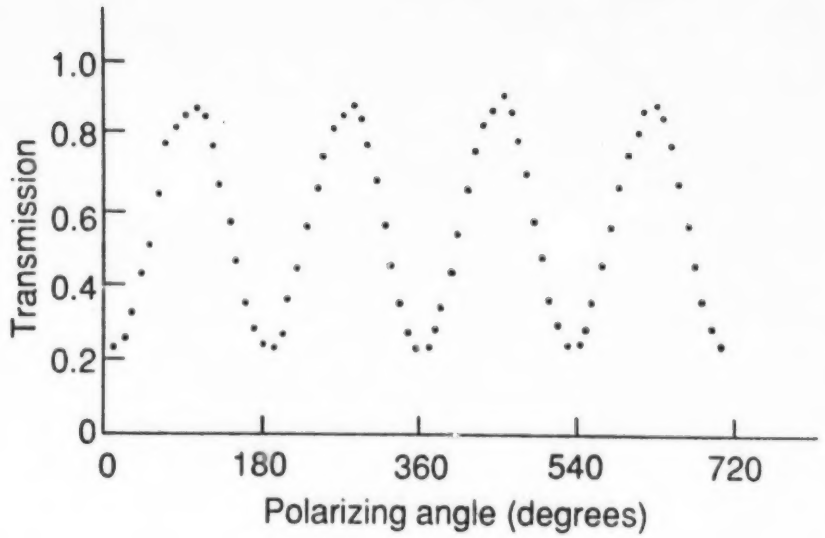

Fig. 7: Polarization effects produced by fiber directionality in a thin sheet of pine wood. The transmissivity is maximum for a laser polarization perpendicular to the wood fibers.

An example of such an analysis is shown in Fig. 10. The material is a polypropylene sheet with nearly 1 mm-long steel fibers of different concentration and orientation. A 0.5 W Argon laser was used to spot heat the black painted sheet for 30 seconds, whose surface temperature was monitored with an AGEMA 782 IR camera. Some isotherm contour images are shown in Fig. 10. The thermographs shown in Fig. 10(a) and (b) correspond to 12% steel concentration, while (c) and (d) show the results obtained with 3% steel-concentration samples. In figures 10(a) and (c) the filler is preferentially oriented in the vertical direction, while (b) and (d) correspond to nominally random-orientation samples. We can see that the filler orientation can be clearly evaluated from the ellipticity of the thermal pattern, particularly in the case of high steel concentration where fiber-to-fiber near-contacts are relatively frequent. Such patterns can be used to evaluate fiber concentration uniformity and local anisotropy by scanning the heating beam over the inspected part.

Moreover, by following the rate of transient thermal propagation during heating and applying image subtraction techniques, the absolute thermal properties of the material, related to the filler concentration, can be evaluated. Such an analysis may be useful, e.g., to detect epoxy-starved areas in graphite-epoxy aerospace panels after autoclave curing[8].

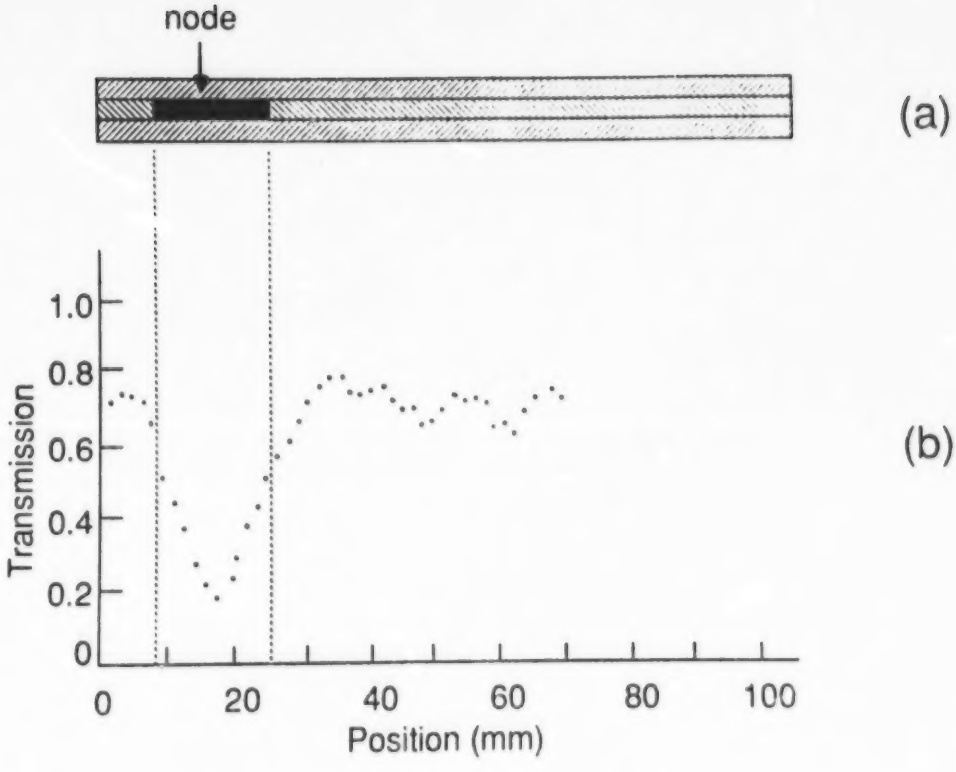

Fig. 8: Detection of a node in a sandwich structure comprising three 3 mm-thick wood sheets; (a): sample structure; (b): spatial scan of the far-IR beam along the wooden laminate.

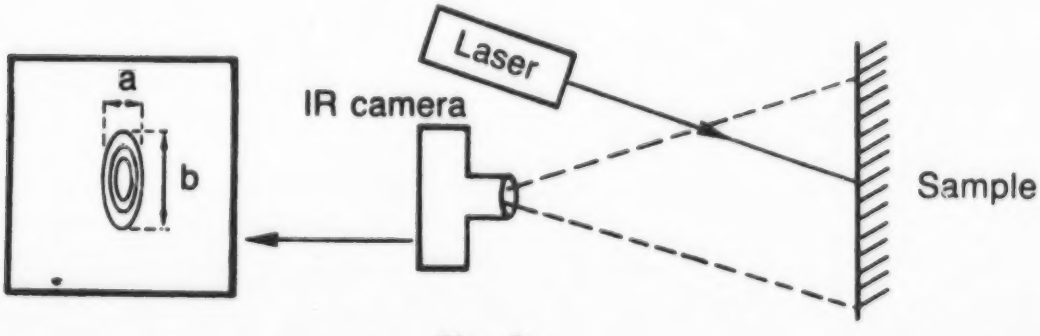

Fig. 9:

Schematic of the apparatus for thermographic analysis of phase orientation in composite materials.

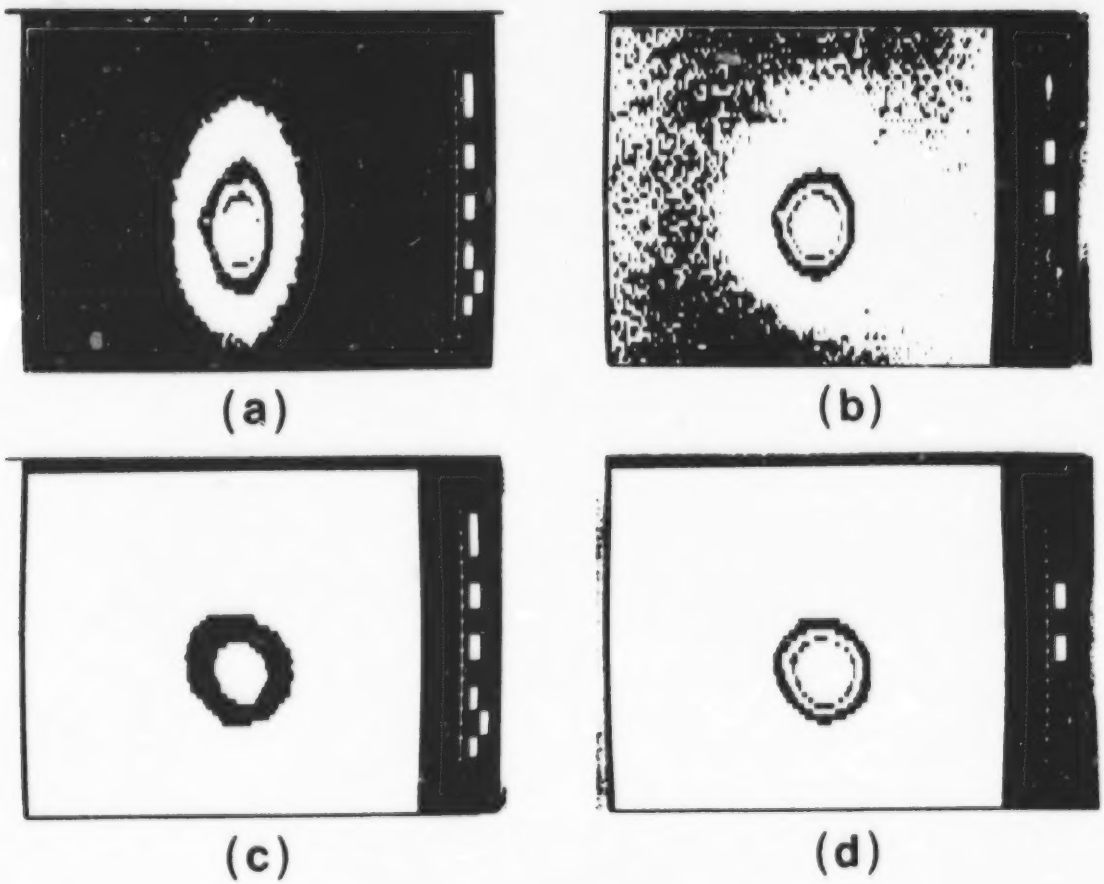

Fig. 10: Thermal patterns obtained with steel-polypropylene sheets with fiber concentration in weight of 12% (a and b) or 3% (c and d) either linearly oriented (a and c) or randomly oriented (b and d). The image areas are typically 5 X 5 cm.

CONCLUSION

Infrared techniques are a powerful approach for a fast, automated and continuous quality control of manufactured materials. They are noncontact, so that they can be implemented with minimum previous sample preparation requirements. Both Far-IR spectroscopic or polarization techniques and infrared thermography techniques have been developed for an analysis of filler concentration and orientation in composite materials. The authors gratefully acknowledge Dr. K. Cole of the Industrial Materials Research Institute, NRCC, in Boucherville, Québec, for the infrared spectrometer, as well as Dr. J.W. Johns, of the Herzberg Institute, NRCC, in Ottawa, Ontario for the Far-IR spectrometer.

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